

36230

Combinations of Technology Useful in a Small Format Film

While the 35 mm negative, with an image area of 24.4 x 36.4 mm, is well established as a standard for quality in amateur photography, there are advantages in employing smaller negative sizes. Commercial examples include the 110 format (image area 13.5 x 19.3 mm) and the Disc format (image size 8.6 x 11.1 mm).

One advantage of a smaller negative format is higher system speed. Photography of a subject at a fixed distance from the camera onto a smaller negative can be accomplished with a shorter focal length lens. To an approximation the image size on the negative is proportional to the lens focal length. For example, the linear image dimension for a 35 mm focal length lens is 0.7 times that of a 50 mm lens for the same subject distance. The system speed is effectively doubled because the f -number can be lower with the 35 mm lens and still maintain depth of field. The reduced lens to film plane distance also enables more compact camera design.

A further benefit of reduced image size of the photographic negative is that the chemical consumption per exposure during photographic processing is less, and consequently the by-products of processing requiring disposal are less.

Because greater demands are placed on the image quality of a smaller negative on enlargement to a standard print size, manufacturers of premium quality films can more easily differentiate their product offerings. The primary photographic sensors in the film are silver halide crystals having a random spatial distribution, so the final image also has a particulate structure. In chromogenic photography using incorporated couplers, the image is formed by coupler-containing hydrophobic droplets dispersed with the silver halide. During development, dye is formed as a cloud of droplets around each crystal. The dye clouds can be seen under magnification and convey a visual sensation of non-uniformity or graininess. It follows that the impression of graininess will increase at the higher magnification required by smaller format negatives. This is somewhat offset by the lower film speed requirements for a given system speed. Nevertheless, any technology in film design useful for reducing perceived graininess is proportionately more important for smaller formats. The objective correlate to graininess is granularity, which is the spatial variation in optical density observed when numerous readings are taken of a uniformly exposed patch of processed film using a densitometer having a very small aperture. The distribution of such measurements approximates to Gaussian and can be characterized by its standard deviation, or Root Mean Square (RMS) granularity.

Sharpness is the ability to discriminate edge detail in the final image. In photography, sharpness may be degraded by camera focus, depth of field, subject movement, camera movement, and the optical properties of the film. In the negative-positive system, printer focus and the optical properties of the photographic paper are also important. Since a smaller negative format also requires a higher magnification of image edges, any film technology helpful in maintaining good edge discrimination will be proportionately more important. The sharpness of a film is usually assessed by its modulation transfer function (MTF), which measures how well sinusoidal patterns of different frequencies are reproduced. The negative size and print size determine the magnification which in turn determines which spatial frequencies are most important. There may be advantages in selectively enhancing certain frequencies with smaller format negatives.

Extreme care must be taken in the manufacture and use of photographic film to prevent unwanted material such as airborne dust becoming attached to the image surface. A higher negative magnification will result in unwanted particulate material becoming more visible in the final image. Similarly, artifacts such as scratches or pressure related marks on the film will be subject to higher magnification, and greater attention must be given to their reduction.

To maintain the same exposure time, higher light intensity is required for the printing of a smaller negative. Alternatively, a longer printing time may be employed, giving reduced printer productivity. In both situations it is desirable that the image dyes in the negative have good light stability, so that reprints will not suffer a deterioration in quality due to dye fade. Also where higher light intensities are used thermal stability may become an issue. It follows that keeping the negative minimum optical density (D-min) as low as possible is important for small format negatives to minimize printer light intensity or exposure time.

It is possible to imagine a range of different products that would benefit from small format negative images. These would include new systems that allow smaller cameras that would be easy to carry, including conventional and single use cameras. Smaller cameras would have advantages in shipping costs and store display space. Having a smaller negative per image also has processing advantages in replenishment rates per image and size of processing equipment required. Storage of smaller negatives, both loose and kept in cartridge, requires less space as well.

It is envisioned that there will be more interface between film and electronic storage and display systems. Small negatives and cartridges that interact with image scanning equipment or home processing equipment may allow smaller designed and therefore more compact systems as a result of smaller negative images. Smaller negatives make it harder for the consumer to see the image on the film. It may be useful to generate a composite print of the

negatives to make it easier for the consumer to reorder specific prints. Such index prints may be an important capability to have when a small format negative is used.

The film designer must select appropriate combinations of technologies that will give optimum characteristics in a given negative format. While the examples of 110 and Disc format are cited above, it is understood that the discussion applies equally well to any negative size less than standard 35 mm. It is the intent of this Research Disclosure to describe appropriate combinations of technologies useful in a small format film.

As is described above, small format films have potential disadvantages which must be overcome in design and manufacture. Specific performance features which can be addressed by the design and composition of the silver halide emulsions include speed, fog, sharpness, granularity, and sensitivity to pressure.

The use of tubular grain optical properties as a function of grain thickness to optimize photographic performance is taught in Research Disclosure 25330 of May 1985 pp 237-240. Emulsions and photographic elements which utilize and expand such teachings are described in U.S. patents 4,672,027; 4,693,964 and 4,748,106.

Tabular grain emulsions can be utilized to provide improved granularity in the photographic image. Representative emulsions are described in the following patents: USP 4,434,226; USP 4,439,520; USP 4,490,458; USP 4,865,964; USP 4,853,322; USP 5,219,720, USP 4,686,176 and EP 534,395.

Silver halide emulsions which have proven to be particularly useful are those of mixed halide content having distinct phases of differing halide composition. Representative examples of this type of emulsion are described in the following references: USP 4,433,048; USP 4,490,458; USP 5,059,51; USP 4,835,095; USP 4,670,735; USP 4,668,614; USP 4,945,037 and GB 2,222,694.

The size frequency distribution of silver halide emulsions is also utilized to provide images having improved characteristics. Representative emulsions reported to be effective in providing improved granularity and/or sharpness are disclosed in the following references: USP 4,686,178; USP 4,762,778; USP 4,728,602 and USP 5,250,403.

Most recently silver halide emulsions comprising high levels of chloride have been prepared of increased photographic speed; the use of such emulsions allows the use of processing which is friendlier to the environment. Emulsions having high chloride content suitable for use in a small format negative include those described in the following references: USP 4,399,215; USP 4,400,463; USP 4,414,306; USP 4,713,323; USP 4,783,398; USP 4,804,621; and USP 4,952,491.

To record blue light it is not essential that spectral sensitizing dyes are employed, since silver bromide and silver iodobromide emulsions have native blue sensitivity. However, it is preferred to use blue spectral sensitizers for tabular grain emulsions. Examples are given in USP 4,439,520. The green and red light recording elements require one or more spectral sensitizing dyes. A summary of generally useful spectral sensitizing dyes is contained in Research Disclosure 308119, Section IV. Additional references for specific combinations of sensitizing dyes in tabular grain emulsions are USP 4,581,329; USP 4,582,786; USP 4,592,621; USP 4,609,621; USP 4,675,279; USP 4,678,741; USP 4,720,451; USP 4,818,675; USP 4,945,036; and USP 4,952,491. It is desirable to have low levels of retained sensitizing dyes after processing to achieve low D-min. Patents that deal with low stain dyes particularly useful for tabular grain emulsions are USP 5,091,298; USP 5,196,299 and USP 5,210,014.

Sensitizing dyes are chosen for optimum photographic sensitivity, optimum color reproduction, stability, and synthetic ease. Dyes may be added before, after, or during the chemical finishing of the emulsion. Preferred and useful sensitizing dyes for small format film include, but are not limited to the following:

Red Sensitizing Dyes that singly or in combination provide maximum sensitivity in the range 600-660 nm are as follows:

Anhydro-5,5'-dichloro-9-ethyl-3,3'-di-(3-sulfopropyl)thiacarbocyanine hydroxide, triethylammonium salt

Anhydro-9-ethyl-5',6'-dimethoxy-5-phenyl-3-(3-sulfobutyl)-3'-(3-sulfopropyl)oxathiocarbocyanine hydroxide

Anhydro-9-ethyl-5,5'-dimethyl-3,3'-di-(3-sulfopropyl)thiacarbocyanine hydroxide, triethylammonium salt

Anhydro-9-ethyl-5',6'-dimethyl-5-phenyl-3-(2-sulfoethyl)-3'-(4-sulfobutyl)oxathiocarbocyanine hydroxide, sodium salt

Anhydro-11-ethyl-1,1'-di-(3-sulfopropyl)naphtho[1,2-d]thiazolocarbo-cyanine hydroxide, triethylammonium salt

Anhydro-5,5'-dichloro-3,9-diethyl-3'-(3-sulfopropyl)thiacarbocyanine hydroxide

Anhydro-5,6-dichloro-1-ethyl-1',3-di-(3-sulfopropyl)benzimidazoloneaphtho[1,2-d]thiazolocarbo-cyanine hydroxide, triethylammonium salt

3,3'-Di-(2-carboxyethyl)-5,5'-dichloro-9-ethylthiacarbocyanine bromide

- Anhydro-9-ethyl-3-methyl-5-phenyl-3'-(3-sulfofopropyl)oxacarbocyanine hydroxide
- 2,4,6(1H,3H,5H)-Pyrimidinetrione, 5-(2-(1-ethylnaphtho[1,2-d]thiazol-2(3H)-ylidene)-1-((1-ethylnaphtho[1,2-d]thiazol-2(3H)-ylidene)methyl)ethylidene)-1,3-bis-(2-methoxyethyl)-1,1',11-triethylnaphtho[1,2-d]thiazolocarbo-cyanine bromide
- Anhydro-3,9-diethyl-5,5'-dimethoxy-3'-(3-sulfofopropyl)thiacarbocyanine hydroxide
- Anhydro-9-ethyl-5,6-dimethoxy-5'-phenyl-3,3'-di-(3-sulfofopropyl)thiacarbocyanine hydroxide, potassium salt
- Anhydro-9-ethyl-5',6'-dimethoxy-5-phenyl-3,3'-di-(3-sulfofopropyl)oxathiacarbocyanine hydroxide, sodium salt
- 2-(2-(4-diethylaminophenyl)ethenyl)benzothiazole
- Green Sensitizing Dyes that singly or in combination provide maximum sensitivity in the range 520-570 nm are as follows:
- Anhydro-5-chloro-9-ethyl-5'-phenyl-3'-(3-sulfofopropyl)-3-(3-sulfofopropyl)oxacarbocyanine hydroxide, triethylammonium salt
- Anhydro-6,6'-dichloro-1,1'-diethyl-3,3'-di-(3-sulfofopropyl)-bis(trifluoromethyl)benzimidazolocarbo-cyanine hydroxide, triethylammonium salt
- Anhydro-11-ethyl-1,1'-di-(3-sulfofopropyl)naphth[1,2-d]oxazolocarbo-cyanine hydroxide, triethylammonium salt
- Anhydro-5-chloro-9-ethyl-5'-phenyl-3'-(2-sulfoethyl)-3-(3-sulfofopropyl)oxacarbocyanine hydroxide, triethylammonium salt
- Anhydro-6,6'-dichloro-1,1'-diethyl-3,3'-di-(4-sulfofopropyl)-5,5'-bis(trifluoromethyl)benzimidazolocarbo-cyanine hydroxide, triethylammonium salt
- Anhydro-9-ethyl-5,5'-diphenyl-3,3'-di-(2-sulfoethyl)oxacarbocyanine hydroxide, sodium salt
- Anhydro-9-ethyl-5-t-pentyl-5'-phenyl-3-(4-sulfofopropyl)-3'-(2-sulfoethyl)oxacarbocyanine hydroxide, triethylammonium salt
- Anhydro-9-ethyl-5,5'-diphenyl-3,3'-di-(4-sulfofopropyl)oxacarbocyanine hydroxide, sodium salt
- 5,5'-Dicyno-1,1',3-triethyl-3'-(4-acetyl-sulfamoylbucyl)benzimidazolocarbo-cyanine bromide
- Anhydro-9-ethyl-5,5'-diphenyl-3,3'-di-(3-sulfofopropyl)oxacarbocyanine hydroxide, sodium salt
- Anhydro-9-ethyl-5,5'-dichloro-3,3'-di-(3-sulfofopropyl)oxacarbocyanine hydroxide, triethylammonium salt
- Anhydro-5,5',6,6'-tetrachloro-1,1',3-triethyl-3'-(3-sulfofopropyl)benzimidazolocarbo-cyanine hydroxide
- Anhydro-3,9-diethyl-5-phenyl-3'-(3-sulfofopropyl)oxacarbocyanine hydroxide
- Anhydro-9-ethyl-5,5'-diphenyl-3,3'-di-(3-sulfofopropyl)oxacarbocyanine hydroxide, sodium salt
- Anhydro-5-chloro-9-ethyl-5'-phenyl-3,3'-di-(3-sulfofopropyl)oxacarbocyanine hydroxide, triethylammonium salt
- Blue Sensitizing Dyes:
- Anhydro-5,5'-dichloro-3,3'-di-(3-sulfofopropyl)thiacyanine hydroxide, triethylammonium salt
- Anhydro-5,5'-dichloro-3,3'-di-(4-sulfofopropyl)thiacyanine hydroxide, triethylammonium salt
- Anhydro-5,5'-dimethoxy-3,3'-di-(4-sulfofopropyl)thiacyanine hydroxide, triethylammonium salt
- Anhydro-5'-methoxy-1,3'-di-(3-sulfofopropyl)naphtho[1,2-d]thiazolothiacyanine hydroxide, sodium salt

Aside from the light sensitive element, there is a range of materials particularly useful for applications in small format systems. Listed below are specific materials that have the desired properties. The photographic scientist has many optimizations to make that will require choices of one material over another depending on the specific film features that are being emphasized. For smaller format negatives image sharpness, graininess, cost, film speed and color reproduction would be the focus of optimization. More will be said about such combination decisions later.

Several structural classes of yellow coupler are particularly useful for small format systems because of their optimized hue, low unwanted absorption, coupling activity, stability, lack of effects on the emulsions, and low process sensitivity. Examples of yellows meeting these requirements are X-1 Benzoic acid, 4-chloro-3-(12-(4-ethoxy-2,5-dioxo-3-(phenylmethyl)-1-imidazolylidyl)-3-(4-methoxyphenyl)-1,3-dioxopropyl)amino)-dodecyl ester and analogs such as X-2 Benzoic acid, 4-chloro-3-(12-(4-ethoxy-2,5-dioxo-3-(phenylmethyl)-1-imidazolylidyl)-4,4-dimethyl-1,3-dioxopentyl)amino)-, dodecyl ester (see also US 5,019,489, US 4,960,685, US 4,022,620), X-3 1-imidazolylideneacetamide, N-(2-chloro-5-

((hexadecylsulfonfyl)amino)phenyl)- α -(2,2-dimethyl-1-oxopropyl)-4-ethoxy-2,5-dioxo-3-(phenylmethyl)- as described in US 4,022,620, Y-4 Pentanamide, N-(2-chloro-5-sulfonfyl)phenyl)-4,4-dimethyl-3-oxo- and analogs described in US 3,933,501, 3,644,498, 3,408,194, Y-5 Benzoic acid, 4-chloro-3-((2-(2,5-dioxo-3-(phenylmethyl)-1-imidazolidinyl)-3-(4-methoxyphenyl)-1,3-dioxopropyl)amino)-, dodecyl ester, Y-6 Benzoic acid, 4-chloro-3-((2-(3,5-dioxo-1-phenyl-2-(phenylmethyl)-1,2,4-triazolidin-4-yl)-4,4-dimethyl-1,3-dioxopentyl)amino)-1-((dodecyloxy)carbonyl)pentyl ester and analogs described in US 4,314,023, Y-7 Benzoic acid, 4-(1-((2-chloro-5-((dodecylsulfonfyl)amino)phenyl)amino)carbonyl)-3-dimethyl-2-oxobutoxy-, 1-methylethyl ester. Also of particular usefulness in films of this type would be the following yellow couplers: Y-8 Pentanamide, N-(2-chloro-5-((hexadecylsulfonfyl)amino)phenyl)-4,4-dimethyl-3-oxo-2-(4-((4-phenyl)sulfonfyl)phenoxy)-, US 3,265,506, US 3,408,194, Y-9 3-Oxalidinediacetamide, N-(5-((2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-2-chlorophenyl)- α -(2,2-dimethyl-1-oxopropyl)-5,5-dimethyl-2,4-dioxo- US 4,314,023, Y-10 1H-1,2,4-triazole-1-acetamide, N-(5-((4-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-2-chlorophenyl)-3-chloro- α -(2,2-dimethyl-1-oxopropyl)-, and Y-11 1H-imidazole-1-acetamide, N-(4-((dimethylamino)sulfonfyl)-2-methoxyphenyl)- α -(4-(hexadecyloxy)benzoyl)-2-((phenylamino)carbonyl)- EP 30,747 (A).

There are specific magenta couplers that are preferred when one is trying to generate a high quality small format film. These must be chosen for their excellent hue, low unwanted absorption, good activity and efficiency, stability, lack of negative effects on the emulsions, minimum process sensitivity and optimized to generate a matched set of dyes with the yellow and cyan for desired color reproduction and neutral scale. Specific compounds that have been identified as being useful for a film system described here include the following couplers: M-1 Dodecanamide, N-(4-(3-(7-chloro-6-methyl-1H-pyrazolo(5,1-c)-1,2,4-triazol-3-yl)propyl)phenyl)-2-(4-(4-hydroxyphenyl)sulfonfyl)phenoxy)- (US 4,443,536), M-2 Benzoic acid, 3-(((4-(1-(7-chloro-6-methyl-1H-pyrazolo(5,1-c)-1,2,4-triazol-3-yl)tridecyl)oxy)phenyl)amino)sulfonfyl)- (US 4,808,502 EP 284,240), M-3 Butanoic acid, 4-((1-(7-chloro-6-methyl-1H-pyrazolo(5,1-c)-1,2,4-triazol-3-yl)tridecyl)octylamino)-4-oxo- (EP application 0,285,274, US 4,808,502), M-4 benzenesulfonamide, N-(1-(7-chloro-6-methyl-1H-pyrazolo(5,1-c)-1,2,4-triazol-3-yl)ethyl)-4-((methylsulfonfyl)amino)-N-octadecyl- (US 4,865,963), M-5 Benzamide, N-(7-chloro-6-methyl-1H-pyrazolo(5,1-c)-1,2,4-triazol-3-yl)-phenylmethyl)-4-((methylsulfonfyl)amino)-N-octadecyl- (D64427), M-6 Tetracanamide, N-(3-((4-(2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)phenylthio)-4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)amino)-4-chlorophenyl)-, M-7 3H-pyrazol-3-one, 4-((2,4-bis(1-methylethyl)phenyl)thio)-5-((2-chloro-4-

(dodecylsulfonfyl)phenyl)amino)-2,4-dihydro-2-(2,4,6-trichlorophenyl)- (US Serial#07/905,052), M-8 Butanamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(4-(4-methoxyphenoxy)-3-((2-(6-(2-phenoxyethoxy)-7-(1H-pyrazol-1-yl)-1H-pyrazolo(1,5-b) (1,2,4)triazol-2-yl)propyl)amino)sulfonfyl)phenyl)- (EP appl. 0,459,349A1, EP appl. 0,428,902A1), M-9 Octanamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(3-((2-(7-chloro-6-methyl-1H-pyrazolo(1,5-b) (1,2,4)triazol-2-yl)propyl)amino)sulfonfyl)-4-(2-ethoxyethoxy)phenyl)-, M-10 Benzanamide, 3-(((2,4-bis(1,1-dimethylpropyl)phenoxy)acetyl)amino)-N-(4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)- (US 2,369,489, US 2,600,788), M-11 Benzanamide, 3-((2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-N-(4,5'-dihydro-5'-oxo-1'-(2,4,6-trichlorophenyl)(1,4'-bi-1H-pyrazol)-3'-yl)- (Kokai 60-035,730), M-12 2-Propanoic acid, butyl ester, polymer with N-(1-(2,5-dichlorophenyl)-4,5-dihydro-5-oxo-1H-pyrazol-3-yl)-2-methyl-2-propenamide (US 4,409,320) and M-13 Polymer derived from 1 part styrene, 1 part butylacrylate and 1 part propene, 2-(N-(4',5'-dihydro-5'-oxo-1'-(2,4,6-trichlorophenyl)(1,4'-bi-1H-pyrazol)-3'-yl)carboxamide (EP 133,262).

The following cyan couplers are particularly useful for small format films because of their good hues, low unwanted absorption, desired coupling activity, good process sensitivity, low leuco dye formation, reasonable dye stability, low effect on emulsion performance and ease of manufacturing. The specific cyan will be chosen based on the optimization of color with the yellow and magenta chosen, reactivity balance with the other couplers, cost, manufacturability, and neutral fade with the other couplers. Cyans identified that would be of particular use would include C-1 Hexanamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(4-(((4-cyanophenyl)amino)carbonyl)amino)-3-hydroxyphenyl), C-2 Hexanamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(4-(((4-cyanophenyl)amino)carbonyl)amino)-5-hydroxy-2-(4-methoxyphenoxy)phenyl)- (US 4,333,999), C-3 Hexanamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(4-(((3,4-dicyanophenyl)amino)carbonyl)amino)-3-hydroxyphenyl)-, C-4 Butanamide, N-(4-(((4-cyanophenyl)amino)carbonyl)amino)-5-hydroxy-2-(4-methoxyphenoxy)phenyl)- (US 4,333,999), C-5 Hexanamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(4-(((4-cyanophenyl)amino)carbonyl)amino)-3-hydroxyphenyl)-3-methyl-2-(tetradecylsulfonfyl)-C-5 Hexanamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(4-(((4-cyanophenyl)amino)carbonyl)amino)-3-hydroxyphenyl)-, C-6 Butanamide, N-(4-(((4-cyanophenyl)amino)carbonyl)amino)-3-hydroxyphenyl)-3-methyl-2-(tetradecylsulfonfyl)-, C-7 Hexanamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(4-(((4-chloro-3-cyanophenyl)amino)carbonyl)amino)-3-hydroxyphenyl)- (US 4,609,619), C-8 Butanoic acid, 4-((4-((3-(1,1-dimethylpropyl)phenoxy)butyl)amino)carbonyl)-4-hydroxy-1-naphthalenyl)oxy)phenyl)-4-oxo- (EP 207,474), C-9 2-Naphthalenecarboxamide, N-(4-(2,4-bis(1,1-dimethylpropyl)phenoxy)butyl)-1-hydroxy-4-(2-(2-methoxyethyl)amino)-2-oxoethoxy)- (US 4,134,766), C-10 Acetic acid, (2-(3-((hexadecylamino)carbonyl)-4-hydroxy-1-naphthalenyl)oxy)ethylthio)- (US 4,296,199), C-11 Carbamic acid,

(6-((3-(dodecyloxy)propyl)amino)carbonyl)-5-hydroxy-1-naphthalenyl)-, 2-methylpropyl ester (US 3,733,651, US 4,690,889), C-12 Acetic acid, ((2-(3-((3-(dodecyloxy)propyl)amino)carbonyl)-4-hydroxy-8-((12-methylpropoxy)carbonyl)amino)-1-naphthalenyl)oxy)ethyl)thio), C-13 Tetradeanoic acid, 2-((2-(3-(butylamino)carbonyl)-4-hydroxy-8-((12-methylpropoxy)carbonyl)amino)-1-naphthalenyl)oxy)ethyl)thio)- (US 4,690,889), and C-14 Carbamic acid, (6-((3-(2,4-bis(1,1-dimethylpropyl)amino)carbonyl)phenoxy)propyl ester. Close analogs also likely to be useful are described in the patents listed.

In order to obtain desired sharpness and color reproduction properties required of a small format film, yellow couplers that release inhibitors are often needed. As stated, sharpness becomes a very critical feature when building a small format negative because of the higher magnification needed to print from the smaller format. These image modifying agents are very critical to obtaining the desired quality in such a product. Preferred yellow dye forming DIR couplers include X-12 Carbamothioic acid, ((2-(1-((5-((4-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-2-chlorophenyl)methyl)ethyl)-, S-(1-ethyl-1H-tetrazol-5-yl) ester (US 4,248,962), X-13 1H-tetrazole-1-acetic acid, 5-(((2-(1-((2-chloro-5-((hexacylsulfonyl)amino)phenyl)amino)carbonyl)-3,3-dimethyl-2-oxobutoxy)-5-nitrophenyl)methyl)ethylamino)carbonyl)thio)-, propyl ester (US 4,477,563, US 4,980,267), X-14 Pentanamide, N-(5-((4-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-2-chlorophenyl)-4,4-dimethyl-3-oxo-2-((1-phenyl-1H-tetrazol-5-yl)thio)- (US 3,265,506), X-15 Pentanamide, N-(2-methoxy-5-(N-methyl-N-dodecylsulfonyl)amino)phenyl-3-(4-(N-(2-hydroxyethyl)sulfonamide)phenoxy)-4,4-dimethyl-3-oxo-, X-16 1H-Benzotriazolecarboxylic acid, 1-(1-((5-((4-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-2-chlorophenyl)amino)carbonyl)-3,3-dimethyl-2-oxobutyl)-, phenyl ester, X-17 Benzotriazolecarboxylic acid, 1(or 2)-((2-(2-chloro-5-((2-(dodecyloxy)-1-methyl-2-oxoethoxy)carbonyl)phenyl)amino)-1-((2-chloro-5-((2-(dodecyloxy)-1-methyl-2-oxoethoxy)carbonyl)phenyl)amino)carbonyl)-2-oxoethyl)-, phenyl ester (US 4,477,563), X-18 1H-tetrazole-1-acetic acid, 5-(((2-(1-((2-chloro-5-((hexacylsulfonyl)amino)phenyl)amino)carbonyl)-3,3-dimethyl-2-oxobutoxy)-5-nitrophenyl)methyl)ethylamino)carbonyl)thio)-, butyl ester (US 4,782,012, US 4,980,267) and X-19 Pentanamide, 3-3-((3-methylbenzothiazolin-2-ylidene)amino)benzotriazole-N-(5-((4-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-2-chlorophenyl)-4,4-dimethyl-3-oxo- (US 4,095,984).

Magenta image modifying couplers that are used to obtain improved color and sharpness include M-14 Butanamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(4-(4,5-dihydro-5-oxo-4-((1-phenyl-1H-tetrazol-5-yl)thio)-3-(1-pyrrolidinyl)-1H-pyrazol-1-yl)phenyl)- (US 3,615,506), M-15 1H-Benzotriazole-6-carboxylic acid, 1-(3-((2-chloro-5-((1-pyrotetradecyl)amino)phenyl)amino)-4,5-

dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-4-yl)-, phenyl ester (US 4,477,563), and M-16 Butanamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(4-(4-(1-ethyl-1H-tetrazol-5-yl)thio)-4,5-dihydro-5-oxo-3-(1-pyrrolidinyl)-1H-pyrazol-1-yl)phenyl)-.

Cyan image modifying couplers used for improved sharpness and color reproduction of particulate value for small format include C-15 Carbamothioic acid, ((2-(4-hydroxy-3-((12-(tetradecyloxy)phenyl)amino)carbonyl)-1-naphthalenyl)oxy)-5-nitrophenyl)methyl(1-methyl)ethyl)-, S-(1-phenyl-1H-tetrazol-5-yl) ester (US 4,248,962), C-16 2-Naphthalenecarboxamide, 1-hydroxy-4-(2-nitro-4-((1-phenyl-1H-tetrazol-5-yl)thio)methyl)phenoxy)-N-(2-(tetradecyloxy)phenyl)- (US 4,409,323), US 4,912,024, and US 4,962,018), C-18 1H-tetrazole-1-acetic acid, 5-(((4-(4-hydroxy-3-((12-(tetradecyloxy)phenyl)amino)carbonyl)-1-naphthalenyl)oxy)-3-nitrophenyl)methyl)thio)-, propyl ester, C-19 Glycine, N-(4-butyl-4,5-dihydro-5-thioxo-1H-tetrazol-1-yl)methyl)-N-((4-hydroxy-3-((12-(tetradecyloxy)phenyl)amino)carbonyl)-1-naphthalenyl)oxy)carbonyl)-, methyl ester C-20 Naphthalenecarboxamide, 4-((1-ethyl-1H-tetrazol-5-yl)thio)-1-hydroxy-N-(2-(tetradecyloxy)phenyl)-, C-21 2-Naphthalenecarboxamide, 1-hydroxy-4-((1-phenyl-1H-tetrazol-5-yl)thio)-N-(2-(tetradecyloxy)phenyl)- (US 3,227,554), C-22 2-naphthalenecarboxamide, 1-hydroxy-4-((1-(4-methoxyphenyl)methyl)-1H-tetrazol-5-yl)thio)-N-(2-(tetradecyloxy)phenyl)-. Compounds described in US 4,421,825 are also of interest in this small format system.

There are times that one wishes to modify an image without generating color by the image modifying coupler. This would be the case if only a single modifier was used in several colored layers for cost advantages, or if a stable image modifying coupler was difficult to generate. In these cases, it is desirable to use "universal" couplers that either do not generate color upon reaction with oxidized developer (Dox), that generate a dye that is washed out during process, or that release image modifying chemistry by some other mechanism than coupling with oxidized developer. For example, undergoing redox reaction with Ag or Dox to generate an intermediate capable of release of the desired image modifying chemistry is described in US 4,618,571 and US 4,985,336. Examples of Universal image modifiers include C-23 1H-tetrazole-1-acetic acid, 5-(((4-(3-(aminocarbonyl)-4-hydroxy-1-naphthalenyl)oxy)-3-((hexacylsulfonyl)amino)phenyl)methyl)thio)-, propyl ester (US 4,782,012, US 5,151,343, US 5,272,043), C-24 Carbamic acid (2-((3-(aminocarbonyl)-4-hydroxy-1-naphthalenyl)oxy)-5-((hexacylsulfonyl)amino)phenyl)methyl-2-nitro-4-((1-phenyl-1H-tetrazol-5-yl)thio)methyl)phenyl ester (EK docket 58905-1) and C-25 2-Naphthalenecarboxamide, 4-(2-((hexacylsulfonyl)amino)-4-((2-nitro-4-((1-phenyl-1H-tetrazol-5-yl)thio)methyl)phenoxy)methyl)phenoxy)-1-hydroxy- (US 5,288,593);

US 5,279,929).

Another way of improving sharpness is to reduce light scatter by having thinner layers. Manufacturing requirements for coating require rheology control of the emulsions coated. This can be accomplished by adjusting the gelatin levels to obtain the optimum rheology, but this often requires a higher level of gelatin that generates thicker coatings. Alternate rheology modifiers have been developed that are used to optimize coating without increase in layer thickness. Specific compounds include 2-acrylamide-2-methylpropane sulfonic acid (Research Disclosure #23406, Oct. 1983), styrene sulfonic acid (EPA 0,439,172 A2) and copolymers of such materials.

It is often necessary to release photographically useful chemicals other than inhibitors from couplers. For example, it is possible to release bleach accelerators from couplers that improve the removal of the silver developed during imaging. This is important to avoid color degradation, reduce Dmin in the processed film, and avoid light scatter from the retained silver that can degrade image sharpness. Particularly useful Bleach Accelerator releasing couplers include C-26 Propanoic acid, 3-((3-((4-2,4-bis(1,1-dimethylpropyl)phenoxy)butyl)amino)carbonyl)-4-hydroxy-1-naphthalenylthio)- (as described in EP 310,125, EP 193,389 and US 4,865,959, and US 4,912,024), M-17 Propanoic acid, 3-((3-((4-2,4-bis(1,1-dimethylpropyl)phenoxy)butyl)amino)carbonyl)-4-hydroxy-1-oxododecyl)amino)phenyl)propyl)-6-methyl-1H-pyrazolo(5,1-c)-1,2,4-triazol-7-yl)thio)- (US 4,443,536, US 4,973,535), and C-27 2-Naphthalenecarboxamide, N-(4-(2,4-bis(1,1-dimethylpropyl)phenoxy)butyl)-1-hydroxy-4-((2-(4-morpholinyl)ethyl)thio))- A particularly useful reference to this group of compounds is EP 0,193,389.

Couplers capable of generating a smeared image would be of value in a small format film where granularity requires reduction in order to improve the image quality. These compounds are of particular value when used in combination with other technology that gives high image sharpness, allowing a sharpness grain compromise to be made. Potentially useful image smearing couplers are described in US 4,420,556. In addition, compounds that have shown particular value for having the desired smearing properties include M-18 Propanamide, N-(4-((2-butoxy-5-(1,1,3,3-tetramethylbutyl)phenyl)thio)-1-(2,5-dichlorophenyl)-4,5-dihydro-5-oxo-1H-pyrazol-3-yl)-2,2-dimethyl-, M-19 Acetic acid, (2-decyl-4-methylphenoxy)-, 3-(3'-((2,2-dimethyl-1-oxopropyl)amino)-4',5'-dihydro-5'-oxo-1'-(2,4,6-trichlorophenyl)(1,4'-bi-1H-pyrazol)-4-yl)propyl ester, C-28 Tetradeanoic acid, 2-((2-(3-(cyclohexylamino)carbonyl)-4-hydroxy-1-naphthalenyl)oxy)ethyl)thio)- and C-29 Tetradeanoic Acid, 2-((2-(3-((cyclohexylamino)carbonyl)-4-hydroxy-1-naphthalenyl)oxy)ethyl)thio)-, (GB 2,141,250A, US 4,705,743, US 4,296,200).

It is also desirable for some applications to coat couplers that are one color before coupling, but that change color upon reaction with oxidized developer. These "masking couplers" are used to mask the unwanted absorption that an image dye has in order to generate a uniform density that can be subtracted out upon printing of the image. These couplers therefore improve the saturation of the final printed image obtained with these films and are an important tool to the film builder. Because these dyes absorb light during the exposure step, they can also be effective at reducing light scatter and improving image sharpness.

Particularly useful yellow or magenta colored couplers that generate cyan dye are chosen based on their effective spectral absorption properties both before and after coupling, photographic activity, and stability include C-30 2,7-Naphthalenedisulfonic acid, 5-(acetylaminio)-3-((4-((3-((4-(2,4-bis(1,1-dimethylpropyl)phenoxy)butyl)amino)carbonyl)-4-hydroxy-1-naphthalenyl)oxy)phenyl)azo)-4-hydroxy-, disodium salt (US 4,141,730, US 3,476,563 (362)), C-31 2,7-Naphthalenedisulfonic acid, 5-(acetylaminio)-3-((4-(2-((3-((3-((2,4-bis(1,1-dimethylpropyl)phenoxy)propyl)amino)carbonyl)-4-hydroxy-1-naphthalenyl)oxy)ethoxy)phenyl)azo)-4-hydroxy-, disodium salt (US 4,138,258), C-32 1H-pyrazole-3-carboxylic acid, 4-((4-((3-((4-(2,4-bis(1,1-dimethylpropyl)phenoxy)butyl)amino)carbonyl)-4-hydroxy-1-naphthalenyl)oxy)phenyl)azo)-4,5-dihydro-5-oxo-1-(4-sulfo)phenyl)-, C-33 Benzoic acid, 2-(3-(aminocarbonyl)-5-((4-(2-((3-((2-heptyl-1-oxoundecyl)oxy)-1-methylethyl)amino)carbonyl)-4-hydroxy-1-naphthalenyl)oxy)ethoxy)phenyl)azo)-6-hydroxy-4-methyl-2-oxo-1(2H)-pyridinyl)-, and dyes disclosed in EP appl. 442,029 and EP appl. 423,727.

Important yellow colored couplers that generate magenta dye include M-20 Benzamide, 3-((2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-N-(4,5-dihydro-4-((4-methoxyphenyl)azo)-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)- (US 2,983,608), M-21 Tetradeanoamide, N-(4-chloro-3-((4-(3,4-dimethoxyphenyl)azo)-4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)amino)phenyl)-2-(3-(1,1-dimethylethyl)-4-hydroxyphenoxy)- (US 2,983,608, US 3,519,429), M-22 Tetradeanoamide, N-(4-chloro-3-((4-(4-(dodecyl)oxy)-3-methoxyphenyl)hydrazono)-4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)amino)phenyl)-2-(3-(1,1-dimethylethyl)-4-hydroxyphenoxy)-, M-23 Tetradeanoamide, N-(4-chloro-3-((4,5-dihydro-4-((4-hydroxy-3-methylphenyl)azo)-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)amino)phenyl)-, 531568 Tetradeanoamide, N-(4-chloro-3-((4,5-dihydro-4-((4-methoxyphenyl)azo)-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)amino)phenyl)- (US 4,163,670, US 3,961,960), M-24 Butanamide, N-(4-chloro-3-((4-(4-(2,2-dimethyl-1-oxopropyl)amino)phenyl)azo)-4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)amino)phenyl)-2-(3-pentadecylphenoxy)- and M-25 Tetradeanoamide, N-(4-chloro-3-((4-(4-(2,2-dimethyl-1-oxopropyl)amino)phenyl)azo)-4,5-dihydro-5-

oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)amino)phenyl)-2-(3-(1,1-dimethylethyl)-4-hydroxyphenoxy)-(DE 2643965 C2) and M-26 Benzamide, 3-((2,4-bis(1,1-dimethylpropyl)phenoxy)acetyl)amino)-N-(4,5-dihydro-4-((4-methoxyphenyl)azo)-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)- (US 3,703,375).

Coupler activity (rate of reaction with oxidized developer), hue, stability towards heat and light and other parameters are all highly dependent on environment. Some important factors are choice of permanent coupler solvent (see US 2,322,027, EPA 0 486 929 A1, or EPA 0 491 317 A1), dispersion droplet size (see US 5,190,851), surfactant (see Brit Pat 1,224,523) and preparation method (oil-in-water [see US 2,322,027], solid particle [see US 4,006,025], etc.). These changes can be used with any of the chemical materials described above to optimize the overall performance of the films.

Interlayer scavengers prevent unwanted interlayer diffusion of oxidized developer that could generate undesired color contamination. In addition, these materials can be used as competitors to deplete oxidized developer in imaging layers, to reduce grain and improve sharpness. These materials are therefore important in designing a small format photographic film. Examples of scavengers that have been shown to be of particular value include S-1 1,4-Benzenediol, 2,5-bis(1,1,3,3-tetramethylbutyl)-, and S-2 1,4-Benzenediol, 2,5-di-sec-dodecyl- (382599 1,4-Benzenediol, 2,5-bis(1-methylundecyl)- (US 3,700,453, US 4,732,845, and US 2,360,290), S-3 Benzenesulfonamide, N,N'-(4-hydroxy-1,3-phenylene)bis(4-(dodecyl)- (US 4,447,523, US 4,205,967), S-4 Dodecanoic Acid, 2-(4-(4-hydroxyphenyl)sulfonyl)phenoxy)-, 2-(4-(4-methylbutoxy)phenyl)hydrazide (US 4,923,787), and S-5 Benzamide, N-(2,5-dihydroxyphenyl)-3,5-bis(2-hexyl-1-oxodecyl)amino)- (US 4,732,845).

Incident and reflected radiation can be absorbed or scattered by incorporating materials for that purpose in the photographic element layers or in the support. Filter materials, typically located in overcoat and interlayers, can trim spectrally or attenuate incident radiation. Antihalation materials, typically located in undercoat and backing layers, can eliminate or diminish reflection (halation) exposure of emulsion layers. Ultraviolet absorbing materials can eliminate or diminish unwanted exposure of emulsion layers to sources of ultraviolet radiation during manufacturing steps, camera exposure, and also during subsequent handling of the photographic elements. The ultraviolet absorbing materials can be incorporated in overcoat layers, interlayers, intralayer, undercoat layers, and/or backing layers. The ultraviolet absorbing and scattering materials function primarily as filter materials and can include the materials cited in Research Disclosure 30819 (1989) as well as methods of their incorporation cited therein. Specifically useful to small format photographic elements are F-1 2-Cyano-3-(4-methoxyphenyl)-2-

propenoic acid, propyl ester, as disclosed in US Patent 3,707,375 and F-2 (3-(Dihexylamino)-2-propenylidenepropenenitrile, as disclosed in US Patent 4,045,229 (Reissue 30,303). The use of these ultraviolet materials is additionally facilitated by novel incorporation methods like solid particle dye dispersions, such as disclosed in EP Application 524,593, and polymer-based filter dyes, such as disclosed in US Patent 5,244,994. Ultraviolet absorbers are also incorporated by solvent or non-solvent dispersion methods.

Process-removable materials capable of selectively filtering the exposing light are of two general classes. The first class comprises readily water soluble dyes that may be added during manufacture to adjust the photographic speed of a given color record or to improve image sharpness. Such dyes equilibrate throughout the film structure during or after the coating operation. Since image sharpness is of particular importance in small format negatives the use of water soluble dyes may be an important design tool. Examples of such dyes may be found in EP appl 286,331; EP Appl 316,013; US 4,833,246; US 4,877,721; EP appl 386,908; US 5,001,043.

The second class comprises preformed dyes that are immobilized in given layers of the multilayer structure, but which are destroyed or washed out during processing. It is necessary to insert a blue light filter under the blue record to remove blue light which would otherwise result in unwanted latent image being formed in the underlying green and red records. The traditional material is Carey Lea silver, a finely dispersed colloidal form of metallic silver which removes most of the light at wavelengths < ca 500 nm. Instead of Carey Lea silver, immobile filter dyes may be used. Examples of useful solid particle dyes are described in USP 4,923,788, such as F-3 N-(4-(4-cyano-2-(2-furanylmethylene)-2,5-dihydro-5-oxo-3-furanyl)phenyl)-1-butanenesulfonamide. In addition to a blue light filter, a green light filter material may be employed under the green light record of the film. This is helpful in improving the spectral separation between the green and red records. Sample materials are described in US 4,855,221. It is frequently further desirable to place dyes which absorb ultraviolet blue, green, red and/or improved light in a layer adjacent to the support for antihalation protection. It is commonly desirable to have these dyes immobile until released on processing. Additional references to useful solid particle dyes are given in US 4,092,168, US 4,294,916, US 4,294,917, US 4,770,984, US 4,803,150, US 4,857,446, US 4,877,721, US 4,900,652, US 4,900,653, US 4,940,654, US 4,948,717, US 4,948,718, US 4,950,586, US 4,988,611, US 4,994,356, E.P.A. 430,186, E.P.A. 434,026, US 5,053,387, E.P.A. 456,163, E.P.A. 457,456, E.P.A. 460,550, E.P.A. 460,616, US 5,098,818, US 5,098,820 and US 5,213,956.

Other classes of immobile dyes that are removed by processing include metal chelated filter dyes (US 3,406,069), polymer mordanted dyes (Brit. 1,278,621, Brit. 1,528,616, Brit. 1,538,943,

US 4,234,677, EP appl. 409,117), latex or solvent incorporated dyes (US 4,420,555, EP appl. 319,999, EP appl. 383,623, EP appl. 412,379), and filter dyes immobilized with blocking groups/ballasts (US 4,923,789, US 5,019,492, US 5,064,752, EP appl. 508,432 and US 5,158,865).

It is often desirable to incorporate dyes in the film that survive the photographic process, primarily to adjust the spectral density to allow for proper color balance during printing. Dyes of value for such applications include dyes performed by the reaction of oxidized developer with cyan, magenta, or yellow couplers. These dyes may be incorporated in the film in the same way as image couplers.

The materials described above not only have inherently good properties, but also can be combined together into a photographic film in ways that maximize the total overall performance. There are many methods and tools that a film builder can use to construct and optimize the properties of the film that are particularly important in a small format. One of the most important features is image structure, which is a combination of subjective attributes such as sharpness, grain, contrast and color at a given photographic speed. The corresponding objective measurements of these are acutance, granularity, gamma and hue/saturation. These attributes are not independent of each other; for example, grain will inherently increase if either sharpness or contrast is increased; conversely, grain will decrease if sharpness or contrast is reduced. Often, these variables can be adjusted or partitioned differently relative to each other but without making any fundamental change in the total degree of available performance. For example, grain can be reduced by increasing the number of developed silver centers (by increased silver laydown), but this also increases contrast which reduces the grain improvement (through the inherent dependence of grain on contrast). Contrast could then be lowered by the introduction of a DIR (development inhibitor releaser) which would restore the grain improvement. However, if the DIR chosen also improved sharpness (by increased diffusion path length of the inhibitor and resulting unsharp masking), then the grain improvement would again be reduced at the gain of improved acutance. It is the relative balance of these effects that can be controlled by judicious use of the materials that result in optimized performance. All of the materials described are suitable for use with these methodologies.

Some of the ways that grain can be manipulated in photographic films are:

- Layer Starvation in which there is an excess of oxidized developer generated relative to available coupler as described in US 3,843,369; 4,145,219; and UK 923,045. In order to maximize this effect, it is often best to use couplers that are very reactive towards Dox. In addition, it may be necessary to

isolate coupler starved layers with interlayers as described in US 4,447,523.

- Multiple layers with different degrees of sensitivity to the same color of light; for example; see US 4,670,375, US 4,564,587, US 4,804,619, US 4,963,465 or US 4,414,308. Two or three layers can be used to allow for full or partial coupler starvation while still maintaining sensitivity over a wide range of available light (sometimes referred to as latitude). This additionally allows levels of additional materials such as DIRs, bleach accelerators, colored couplers and other materials to be distributed between the layers so as to maximize performance. It is sometimes advantageous to avoid using either DIRs (for example, see US 4,145,219) or colored couplers in the more light sensitive layers. It is also common to use different couplers or mixtures of different couplers in the separate layers in which properties such as hue or activity are adjusted; for example, see US 4,681,837, US 4,963,465, EP 0,467,327-A1, EP Application 0,377,910, EP Application 0,329,016-A2 or EP 0,467,327A1 or US 4,600,688.
- Smearing Couplers; for example see US 4,567,135, US 4,705,743, US 4,543,323 or US 4,420,556.
- Coupler Dispersions with small particle size.
- Less active couplers, particularly with increased levels of silver laydown.
- Combinations of bleach accelerators and image modifiers; for example see US 4,912,024.

Some of the ways that acutance can be manipulated are:

- Image-modifiers that release weak inhibitors that have high diffusibility as described in US 4,414,308; US 4,762,778, US 4,434,225; US 4,528,263; US 4,725,529; US 4,746,600 and US 4,760,016.
- Image-modifiers that have longer timing or delayed release of the inhibitor moiety.
- Image-modifiers that have more soluble and diffusible timing groups that delay inhibitor release so as to increase diffusion path length such as US 4,963,465.
- Image-modifiers that rely on a second separate redox reaction in order to release inhibitor such as the hydroquinone based redox DIR described in EP 537659-A1.
- High activity couplers, so that high levels of image-modifiers can be used while still maintaining adequate contrast such as US 4,963,465.

- Increasing a layer's ability to have its contrast reduced by release of an inhibitor from another layer ('receivership'), since an inhibitor delivered from another layer will have an increased diffusion pathway compared to an inhibitor released within the layer itself.

This can be accomplished by adjusting the inherent sensitivity of the emulsions to inhibitors or by judicious choice of image coupler and/or other film components; for example see US 4,959,299.

The overall hue and saturation of a developed film depends not only on the inherent hues of the individual dyes that make up the image, but also the degree to which each color record affects the others during development. For example, if less yellow dye is formed when the magenta dye is also formed as compared to when no magenta dye is formed, then the color purity of the magenta will be increased (less blue unwanted absorbance) in the case where both dyes are formed. This type of color correction is called interimage. Some of the ways that interimage can be manipulated are:

- Colored Masking Couplers
- Image-modifiers that release weak inhibitors that have high diffusibility as described previously.
- Image-modifiers that have longer timing or delayed release of the inhibitor moiety.
- Image-modifiers that have more soluble and diffusible timing groups that delay inhibitor release so as to increase diffusion path length.
- Image-modifiers that rely on a second separate redox reaction in order to release inhibitor such as the hydroquinone based redox DIR described in EP 537659-A1. (Note that the four above depend on having the image-modifier in a different layer.)
- Improved receivership
- 'Wrong' couplers (couplers that form a different color than expected based on the layer sensitivity; i.e. a cyan coupler in a blue sensitive, yellow dye forming layer. This adjusts interimage as to prevent over-correction; for example, see US 4,273,861.
- Appropriate adjustment of the relative activity difference between coupler(s) and image-modifier(s) in another layer. For example, a high activity (relative to image coupler) image-modifier will release its inhibitor relatively early in the process, thus allowing for increased opportunity for diffusion into another layer while that layer is still developing and able to be inhibited, thus increasing interimage.

- Barrier layers such that diffusion of inhibitor between layers or in and out of the film is controlled. These can be organic in nature, i.e. polymeric as described in USP 5,254,441, or consist of finely divided silver particles such as the so-call "Lipman" emulsion.

Mixtures or combinations of different inhibitor classes or types chosen to adjust interlayer versus intralayer effects. In addition, inhibition effects in a certain layer can be modified by the presence of other materials such as bleach accelerator releasing couplers; for example see US 4,912,024.

- Iodide gradient effects, such that iodide released as a development by-product in one layer affects development in another.

For proper tone scale reproduction, a small format film should have a long latitude with linear response to light over most of its sensitivity range. Some ways to control densities and interimage effects as a function of exposure are:

- Coupler activity, either by mixtures of couplers or by adjustment of their environment.
- Image-modifier placement.
- Colored coupler placement.
- Relative sensitivity of light between each individual emulsion that makes up a color record.
- Degree of relative response to inhibitor of each individual emulsion that makes up a color record.
- Coupler 'borrowing' in which dye is generated in one layer from Dox generated in another.

Small format films may undergo high amounts of physical stress so that it is important that such stress do not affect the photographic performance. Blue sensitive layers are particularly prone to physical stress such as pressure or kinking because of its location near the surface of the film. Some methods used to control physical sensitivity are:

- Emulsions that are inherently less sensitive to pressure, etc. as described in USP 4,826,758; USP 5,190,855; USP 5,061,616; USP 4,616,711; USP 5,068,173; EP 460,656 and EP 547,912.

- Protective layers or materials that help shield or protect the emulsion layer as described in G. F. Duffin, Photographic Emulsion Chemistry, Focal Press, London and New York 1966, pp. 166-168.

- In-camera mechanisms and film transport system.

The following multilayer structures illustrate how the described component technologies may be combined effectively into a small format color negative film. The silver halide emulsions are selected from those referenced earlier such that granularity and acutance are favorable for the intended degree of magnification. The optimum component laydowns may be determined experimentally by a film designer skilled in the art.

Structure 1

Layer	Component	Function
Overcoat		
Interlayer	F-1, F-2	UV Filters
Fast Yellow	Y-1	Yellow Coupler
Mid Yellow	Y-2	Yellow Coupler
Slow Yellow	Y-13	DIR Coupler
Interlayer	Y-2	Yellow Coupler
Fast Magenta	Y-13	DIR Coupler
Mid Magenta	Carey Lea Silver	B Filter
Slow Magenta	S-3	DOX Scavenger
Interlayer	M-2	Magenta Coupler
Fast Cyan	M-14	DIR Coupler
Mid Cyan	M-22	Masking Coupler
Slow Cyan	M-4	Magenta Coupler
Interlayer	C-23	DIR Coupler
Fast Magenta	M-22	Masking Coupler
Mid Magenta	M-4	Magenta Coupler
Slow Magenta	C-23	DIR Coupler
Interlayer	M-17	Bleach Accelerator
Fast Cyan	S-3	DOX Scavenger
Mid Cyan	C-2	Cyan Coupler
Slow Cyan	C-17	DIR Coupler
Interlayer	C-30	Masking Coupler
Fast Magenta	C-1	Cyan Coupler
Mid Magenta	C-17	DIR Coupler
Slow Magenta	C-30	Masking Coupler
Interlayer	C-26	Bleach Accelerator
Fast Cyan	C-1	Cyan Coupler
Mid Cyan	C-26	Bleach Accelerator
Slow Cyan		
Antihalation Underlayer		

Structure 2

Layer	Component	Function
Overcoat		
Interlayer	F-1, F-2	UV Filters
Fast Yellow	Y-1	Yellow Coupler
Mid Yellow	Y-1	Yellow Coupler
Slow Yellow	Y-17	DIR Coupler
Interlayer	Carey Lea Silver	B Filter
Fast Magenta	M-8	Magenta Coupler
Mid Magenta	M-13	Magenta Coupler
Slow Magenta	Y-17	DIR Coupler
Interlayer	M-23	Masking Coupler
Fast Cyan	M-13	Magenta Coupler
Mid Cyan	Y-17	DIR Coupler
Slow Cyan	M-23	Masking Coupler
Interlayer	S-5	DOX Scavenger
Fast Magenta	C-12	Cyan Coupler
Mid Magenta	C-19	DIR Coupler
Slow Magenta	C-11	Cyan Coupler
Interlayer	C-19	DIR Coupler
Fast Cyan	C-31, C-33	Masking Couplers
Mid Cyan	C-11	Cyan Coupler
Slow Cyan	C-19	DIR Coupler
Interlayer	C-31, C-33	Masking Couplers
Antihalation Underlayer		

Structure 3

Layer	Component	Function
Overcoat		
Interlayer	F-1, F-2	UV Filters
Fast Yellow	Y-1, Y-2	Yellow Couplers
	Y-13	DIR Coupler
	C-26	Bleach Accelerator
Slow Yellow	Y-1, Y-2	Yellow Couplers
	Y-13	DIR Coupler
	C-16	DIR Coupler
	C-26	Bleach Accelerator
Interlayer	F-3	B Filter
	S-1	DOX Scavenger
Fast Magenta	M-6	Magenta Coupler
	M-14	DIR Coupler
	M-21	Masking Coupler
Mid Magenta	M-6	Magenta Coupler
	C-16	DIR Coupler
	M-21	Masking Coupler
Slow Magenta	M-6	Magenta Coupler
	M-21	Masking Coupler
Interlayer	S-1	DOX Scavenger
Fast Cyan	C-1	Cyan Coupler
	C-17	DIR Coupler
	C-30	Masking Coupler
	Y-2	Yellow Coupler
Mid Cyan	C-1	Cyan Coupler
	C-17	DIR Coupler
	C-30	Masking Coupler
	C-26	Bleach Accelerator
Slow Cyan	C-1	Cyan Coupler
	C-26	Bleach Accelerator
Antihalation Underlayer		

The sample structures given illustrate several of the points made earlier relating to combinations of technologies. For example, the yellow pack can consist of two (Structures 2, 3) or three (Structure 1) separate imaging layers. More than one yellow imaging coupler may be used. In Structure 3, the yellow pack contains two yellow image couplers and a yellow DIR. It also contains two cyan-dye-forming moieties -- the DIR coupler C-16 and the bleach accelerator C-26. The former provides blue-onto-green interimage while both reduce the extent of blue-onto-red

interimage by generating small amounts of cyan dye in the blue record.

The magenta packs shown all consist of three separate layers. The imaging coupler used in the fast layer may be different from that in the mid and slow layers (Structures 1,2). Structure 1 illustrates the use of the "universal" DIR coupler C-23 in the magenta pack. In Structure 3 a cyan-dye-forming DIR (C-16) is shown in the magenta pack. In spite of generating some unwanted cyan density, this can be an effective tool for green-onto-red and green-onto-blue interimage. For adequate removal of developed silver in the bleach step it may be advantageous to employ a magenta-dye-forming bleach accelerator releasing coupler in the slow magenta layer (Structure 1). Depending on the green-onto-blue interimage needs a yellow colored, magenta-dye-forming masking coupler may be distributed among the three magenta layers. Other choices can be made in magenta pack chemistry with similar results to the selections indicated. The selections and levels are made based on the desire to minimize granularity throughout the exposure scale while preserving the interimage effects necessary for good color. It is understood that high interimage effects and high chemical acutance are strongly correlated.

The choices made in the cyan layers are motivated by similar criteria. Removal of developed silver during the bleach step is most problematic for the cyan layers because they are at the bottom of the multilayer. This is alleviated by appropriate substitution of a bleach accelerator coupler such as C-26 (Structures 1, 3). Structure 2 shows two masking couplers in the cyan pack -- one is yellow colored and the other is magenta colored. These influence red-onto-blue and red-onto-green interimage effects respectively. When it is desired to reduce the extent of red-onto-blue interimage, small amounts of a yellow coupler such as Y-2 may be used selectively in the cyan layers (Structure 3).

The base on which the multilayer is coated is very important when trying to optimize a small format system. The thinner the base, the less light scatter will occur. However, the base must be rigid enough to act as a good support and be strong enough to prevent tearing and breaking during handling and processing. Together with the balance of coatings on the support the film must be resistant to curl so that little distortion occurs during picture taking and during printing of the image. Examples of mordants that meet these requirements include diaxially oriented polyester films such as polyethylene terephthalate (PET) and polyethylene naphthalate (PEN).

In choosing a base for the small format system, the base must have a desired clarity, and little to no color density. Ideally, it should allow no light piping that would cause the film to be fogged. Often it is necessary to incorporate absorber dyes into the base to protect the emulsions from light piping. The amount needed will be influenced by the refractive index of the polymer.

The stiffness of a film is measured by the modulus of the polymer. Useful modulus for a base is between 600 and 1200KSI. Such a Modulus will help control humidity curl amplitude which is important for a small format system.

The base material should also produce low levels of core-set under typical storage and handling conditions. This is particularly important in small format systems because of the need to wind the film onto a small roll to fit in the smaller camera format. High film curl after unwinding may adversely affect film transport and handling during processing and printing. Low core-set can be achieved by selecting materials with a high glass transition temperature, T_g (typically > 100C) and through proper sub-T_g annealing of the support or the coated film (US 4,141,735). The film base should be chemically inert for improved keeping, have no or low low molecular weight oligomers in order to prevent surface defects caused by sublimation, and have low diffusion coefficients for penetrants in order to be resistant to solvent coating needs. Finally, it needs to have proper fracture behavior to allow cutting without generation of dirt or extensive wear on cutting tools.

The bases described above have properties that meet many of the above requirements for a small format film and would be logical choices for such a system.

A base often requires some surface treatment in order to allow good adhesion in the coating of subsequent layers. These "Subbing" treatments may differ for a different base materials. Example methods of subbing include the application of an undercoat layer onto the base material either before or after orientation of the base. Undercoat layers well known in the art comprise, for example, vinylidene chloride/methyl acrylate/itaconic acid terpolymer or vinylidene chloride/acrylonitrile/ acrylic acid terpolymer as described in US 2,627,089, US 2,698,235, US 2,698,240, US 2,943,937, US 3,143,421, US 3,201,249, US 3,271,178, and US 3,501,301. Often the surface of the base is treated by corona or glow discharge, or flame or chemical treatment prior to application of the undercoat layer. Patents that describe useful approaches are US 2,632,931, US 2,648,097, US 2,746,084, US 3,755,683, US 3,761,299, and US 4,717,516. Undercoat layers that may be used in conjunction with surface treatments are described in US 4,394,442, US 4,689,359, US 4,695,532, US 4,429,032, US 4,123,277, US 4,423,089, and US 4,571,379, for example.

It is also very important that a layer be placed on the film that allows the conduction of static discharge. This avoids the fogging of films due to static charge. Example antistat layers are described in the following patents: US 4,070,189, US 4,203,769, US 4,237,194, US 4,701,403, US 4,275,103, US 4,495,276, and US 4,394,441.

The resistance of these layers to scratching is important to prevent defects from forming in the image. Good scratch resistance is very critical to a small format film because of the amplification of the defect during printing. A variety of technologies have been developed to improve scratch resistance on the film back. Film backing layers may comprise various lubricants and matte particles for improved surface lubricity as described in US 3,264,136 and US 4,409,322, for example. It is also known to incorporate inorganic fillers to improve scratch resistance as described, for example, in US 4,675,278 and US 4,500,669. Film backing layers comprising thermally or radiation cured polymers have been reported in US 4,049,861, US 4,310,600, and US 4,957,947.

It may be desirable that information of the picture taking event be recorded on the film in order to improve the processing of the film, and to give record keeping information to the customer. One way to do this is to coat a magnetic layer on the film that can be used to record such information. Materials and procedures that give high quality coatings that meet the requirements of the small format film are described in Research Disclosure November 1992, pg 869, 34390.

Disclosed Anonymously
36230